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Supplement

Table I. Thermochemical data (taken from [38]) and calculated thresholds for the transitions observed experimentally. $\Delta_f H_g^\circ(X)$—standard enthalpy of formation of X in the gas phase, $D(Y\text{-}X)$—dissociation energy, $E_{th}(X(A))$—thermodynamic threshold energy of the appearance of fragment X in the state A.

$\Delta_f H_g^\circ(CH_4) = -74.87$ kJ/mol
$\Delta_f H_g^\circ(CH_3) = 145.69$ kJ/mol
$\Delta_f H_g^\circ(CH_2) = 386.39$ kJ/mol
$\Delta_f H_g^\circ(CH) = 594.13$ kJ/mol
$\Delta_f H_g^\circ(H) = 217.998 \pm 0.006$ kJ/mol
$\Delta_f H_g^\circ(C) = 716.68 \pm 0.45$ kJ/mol
$\Delta_f H_g^\circ(H_2) = 0$ kJ/mol

H excitation energies:
H(1→2) → 10.2 eV
H(2→3) → 1.9 eV
H(3→4) → 0.65 eV
H(4→5) → 0.31 eV
H(5→6) → 0.16 eV
H(6→7) → 0.103 eV
H(7→8) → 0.065 eV
H(8→9) → 0.045 eV

CH_3 + H
$\Delta_f H_g^\circ(CH_3) = \Delta_f H_g^\circ(CH_4) - \Delta_f H_g^\circ(H) + D(CH+H+H_2)$
145.69 kJ/mol = –74.87 kJ/mol – 217.998 kJ/mol + $D(CH+H+H_2)$
$D(CH_3+H) = 438.558$ kJ/mol = 4.545 eV

$CH_3(X) + H(n=3) \rightarrow 16.645$ eV
$CH_3(X) + H(n=4) \rightarrow 17.295$ eV
$CH_3(X) + H(n=5) \rightarrow 17.605$ eV
$CH_3(X) + H(n=6) \rightarrow 17.765$ eV
$CH_3(X) + H(n=7) \rightarrow 17.868$ eV
$CH_3(X) + H(n=8) \rightarrow 17.933$ eV
$CH_3(X) + H(n=9) \rightarrow 17.978$ eV

CH + H + H_2
$\Delta_f H_g^\circ(CH) = \Delta_f H_g^\circ(CH_4) - \Delta_f H_g^\circ(H) - \Delta_f H_g^\circ(H_2) + D(CH+H+H_2)$
594.13kJ/mol = –74.87kJ/mol – 217.998 KJ/mol + 0 kJ/mol + $D(CH+H+H_2)$
$D(CH+H+H_2) = 886.998$ kJ/mol = 9.13 eV

$CH(X) + H_2 + H(n=3) \rightarrow 21.23$ eV
$CH(X) + H_2 + H(n=4) \rightarrow 21.88$ eV
$CH(X) + H_2 + H(n=5) \rightarrow 22.19$ eV
$CH(X) + H_2 + H(n=6) \rightarrow 22.35$ eV

$CH(X) + H_2 + H(n=7) \rightarrow 22.453$ eV
$CH(X) + H_2 + H(n=8) \rightarrow 22.518$ eV
$CH(X) + H_2 + H(n=9) \rightarrow 22.563$ eV

$CH(A) + H+H_2 - 9.13 + 2.88(430\text{ nm}) = 12.01$ eV
$CH(B) + H+H_2 - 9.13 + 3.20(387.2\text{ nm}) = 12.33$ eV
$CH(C) + H+H_2 - 9.13 + 3.95(314\text{ nm}) = 13.08$ eV

CH + 3H
$\Delta_f H_g^\circ(CH) = \Delta_f H_g^\circ(CH_4) - 3.\ \Delta_f H_g^\circ(H) + D(CH+3H)$
$594.13\text{kJ/mol} = -74.87\text{kJ/mol} - 3x217.998\text{ kJ/mol} + 0\text{ kJ/mol} + D(CH+3H)$
$D(CH+3H) = 1322.994\text{ kJ/mol} = 13.71$ eV

$CH(A) + 3H \rightarrow 13.71 + 2.88(430\text{nm}) = 16.59$ eV
$CH(B) + 3H \rightarrow 13.71 + 3.20(387.2\text{nm}) = 16.91$ eV
$CH(C) + 3H \rightarrow 13.71 + 3.95(314\text{nm}) = 17.66$ eV

CH_2 + H + H
$\Delta_f H_g^\circ(CH_2) = \Delta_f H_g^\circ(CH_4) - 2\ \Delta_f H_g^\circ(H) + D(CH+H+H_2)$
$594.13\text{ kJ/mol} = -74.87\text{ kJ/mol} - 2x217.998\text{ KJ/mol} + D(CH+H+H_2)$
$D(CH_2+2H) = 897.256\text{ kJ/mol} = 9.299$ eV

$CH_2(X) + H + H^*(n = 3) \rightarrow 21.399$ eV
$CH_2(X) + H + H^*(n = 4) \rightarrow 22.049$ eV
$CH_2(X) + H + H^*(n = 5) \rightarrow 22.359$ eV
$CH_2(X) + H + H^*(n = 6) \rightarrow 22.519$ eV
$CH_2(X) + H + H^*(n = 7) \rightarrow 22.622$ eV
$CH_2(X) + H + H^*(n = 8) \rightarrow 22.687$ eV
$CH_2(X) + H + H^*(n = 9) \rightarrow 22.732$ eV

CH^+
$E_{th}(CH^+(B)) \rightarrow E_{th}(CH(X)) + IE(CH) + E_{th}(CH(A)) + E_{th}(CH(B))$
$E_{th}(CH^+(B)) = 9.13 + 10.64 + 2.94(422\text{ nm}) + 3.54(350\text{ nm})\text{ eV} = 26.25$ eV

CI
$\Delta_f H_g^\circ(C) = \Delta_f H_g^\circ(CH_4) - 2\ \Delta_f H_g^\circ(H_2) + D(H_2+H_2)$
$716.68 = -74.87\text{kJ/mol} + D(H_2+H_2)$
$D(H_2+H_2) = 716.68 + 74.87 = 791.55\text{ kJ/mol} = 8.20\text{eV}$
$E_{th}(CI\ (3s(^1P^\circ))) = 8.20 + 5.0\text{ eV} = 13.2$ eV

$\Delta_f H_g^\circ(C) = \Delta_f H_g^\circ(CH_4) - 2\ \Delta_f H_g^\circ(H) + \Delta_f H_g^\circ(H_2) + D(2H+H_2)$
$716.68 = -74.87 + 2x\ 217.998 + D(2H+H_2)\text{ kJ/mol}$
$D(2H+H_2) = 716.68 + 74.87 + 2x217.98 = 1227.51\text{ kJ/mol} = 12.72\text{eV}$
$E_{th}(CI\ (3s(^1P^\circ))) = 12.72 + 5.0\text{ eV} = 17.72$ eV

$\Delta_f H_g^\circ(C) = \Delta_f H_g^\circ(CH_4) - 4\ \Delta_f H_g^\circ(H) + D(4H)$

716.68 = –74.87kJ/mol + 2x 217.998 + *D(4H)*
D(4H) = 716.68 + 74.87 + 4 x 217.98 = 1663.47 kJ/mol= 17.24eV
E_{th}(CI ($3s(^1P°)$)) = 17.24 +5.0 eV = 22.24 eV

Supplement

Figure I. Photon yield of transitions measured as a function of the initial electron energy not shown in the paper. Observed thresholds obtained using the fitting method in the measured energy range are indicated by arrows.